

WHAT IF CHONDRITIC POROUS INTERPLANETARY DUST PARTICLES ARE NOT THE REAL McCoy?

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To select a target comet for a Comet Nucleus Sample Return Mission [CNSRM] it is necessary to have an experimental data base to evaluate the extent of diversity and similarity of comets. For example, the physical properties (e.g., low density) of chondritic porous [CP] interplanetary dust particles [IDPs] are believed to resemble these properties of cometary dust¹ although it is yet to be demonstrated that the porous structure of CP IDPs is inherent to presolar dust particles stored in comet nuclei. Porous structures of IDPs could conceivably form during sublimation at the surface of active comet nuclei². Porous structures are also obtained during annealing of amorphous Mg-SiO smokes which initially forms porous aggregates of olivine + platy tridymite and which, upon continued annealing, react to fluffy enstatite aggregates³. It is therefore uncertain that CP IDPs are entirely composed of unmetamorphosed presolar dust. Conceivably, new minerals and textures may form *in situ* in nuclei of active comets as a function of their individual thermal history.

CP IDPs include loosely packed aggregates (<50 μm in size) of many thousands of grains, usually <0.1 μm in size, of variable chemistry and structural state⁴ and fluffy aggregates of granular units (1-2 μm in size) forming a matrix for platy and euhedral single crystals. The chondritic nonporous, granular units consist of ultrafine-grained (0.002 - 0.1 μm in size) platy Mg-rich silicates, sulfides and oxides in carbonaceous material^{5,6}. A broad classification scheme includes (1) olivine- and pyroxene-rich (= anhydrous) IDPs and (2) layer silicate (= hydrated) IDPs, layer silicates occur in several anhydrous CP IDPs^{4,5}. The mineralogy, texture and volatile element enrichments of chondritic IDPs differ distinctly from carbonaceous chondrite matrix and suggest that IDPs are Solar System materials derived from a heliocentric distance >~1.8 AU^{4,7}. The Mg/[Mg+Fe] distributions in anhydrous IDPs^{5,6} are similar to this distribution in Comet Halley dust⁸ and while a link between CP IDPs and comet dust is still tenuous, I will assume that anhydrous CP IDPs are samples of cometary origin.

Traditionally, petrologists have regarded comet nuclei as static environments that preserve unmetamorphosed presolar dust for ~4,550 My. By inference, physical models for active comet nuclei must also constrain environments that will be conducive to mineralogical activity. A recent nucleus model⁹ postulates three different dust environments: (1) porous refractory boulders cemented in (2) an ice-dust matrix and (3) a low-albedo dust mantle. The thermal history of a nucleus includes (1) internal heating (e.g. decay of Al^{26}), (2) surface heating at perihelion and (3) transient events such as devitrification of amorphous water ice and thermally activated release of stored chemical energy¹⁰. Mineralogical activity in ice-dust mixtures requires a thermal regime in excess of ~200K for hydrocryogenic alterations to occur in interfacial water layers at dust-ice interfaces^{11,12}. The high (~330K) average surface temperature of Comet Halley's nucleus during perihelion probably supports a thermal gradient for a sufficiently long period (~100 days) to allow *in situ* hydrocryogenic alterations to occur. Depending on the physical properties, similar conditions may exist in nuclei of other short-period comets during perihelion passage. For this discussion, I concentrate on perihelion heating as similar conditions may occur during trans-Earth flight (typically ~1250 days) in improperly curated comet nucleus samples.

COMET DUST ANALOGS. Mineralogical and structural analyses of granular units in CP IDPs show that (1) grains < ~0.03 μm in size form (sub-) rounded grains, (2) larger grains form thin, sub- to euhedral platy crystals and (3) the platy crystals are regularly embedded in carbonaceous material¹³. These observations have been interpreted as due to annealing of amorphous chondritic precursor material⁶ and I conclude that unmetamorphosed dust in comets has (1) a chondritic composition and (2) is structurally amorphous⁶. A revised norm calculation¹⁴ of CP IDPs¹⁵ shows a nepheline-normative mineralogy including forsterite, feldspar [$\text{Na}/(\text{Na}+\text{Ca}) = 0.91$], FeS and chromite. Thermal annealing, or devitrification, of amorphous precursor dust produces ultrafine-grained (modal size = 0.015 μm) minerals⁶. The ultrafine grain size of minerals formed in this manner in CP IDPs will be most susceptible to aqueous alterations^{16,17}.

DEVITRIFICATION, or uncontrolled crystallisation, of amorphous material can produce a crystalline product with a wide range of chemical compositions, mineralogy and texture. In general, devitrification produces the kinetically most favourable crystalline phases rather than those involving the greatest reduction in free energy which implies the formation of solids that are structurally or chemically similar to the amorphous precursor. Factors influencing devitrification are cooling rates, presence of nucleants (e.g. transition metal ions), precursor viscosity, density of nuclei, chemical concentrations, diffusion rates, orientation and distribution of growing crystals, presence of gases or aqueous solution^{18,19}. Devitrification involves three stages (1) an induction period during which phase separation may occur, (2) (initial) rapid growth and (3) slow growth and coarsening²⁰. In the induction period, amorphous phase decomposition or crystallisation occurs via either homo- or heterogeneous nucleation at the surface of, or within, the amorphous phase¹⁸. The relative amount of phases crystallised are controlled to a large extent by the original precursor composition and the stoichiometry of the phases crystallising from the precursor¹⁸ although a non-stoichiometric phase may initially crystallise as a function of precursor composition and its previous history²¹.

HYDRATION RATES. Experimental data show that hydration rates for silicates increase as a function of (decreasing) grain size^{16,17} is used to evaluate hydration rates for ultrafine grained minerals in granular units of CP IDPs. At this point, I can only extrapolate the data to include nanometer size grains but the results dramatically show the vulnerability of ultrafine-grained silicates to aqueous alterations. For example, at 0.5 kbar and 293K serpentinisation of forsterite decreases from 0.27My (grains 50mm in diameter) to 540 years for grains 0.1 mm in diameter¹⁷. Extrapolation of this data to grains 0.015µm in diameter shows a reduced reaction time of 18 days while a reaction time of ~1 month is found by tentative extrapolation to 200K for these ultrafine grains. Hydration reactions involve lattice and grain boundary diffusion and it is therefore necessary to evaluate diffusion at hydrocryogenic temperatures. The compensation law is used to evaluate the effective lower limit for diffusion in silicates and glasses as a function of grain size²². I calculate that diffusion processes with activation energy less than ~85.0 kJ.mole⁻¹ will cease to operate at 200K in grains 0.015µm, in diameter. Examples of activation energies that meet this criterion include diffusion of Na, K, H, D and He in silicate glasses^{23,24}.

CONCLUSIONS. Unmetamorphosed comet dust is probably structurally amorphous. Thermal annealing of this dust can produce ultra fine-grained minerals and this ultrafine grain size of CP IDPs should be considered in our assessments of aqueous alterations that could affect presolar dust in comet nuclei between 200 and 400K. Devitrification and hydration may occur *in situ* in ice-dust mixtures and the mantle of active comet nuclei. Devitrification, or uncontrolled crystallisation, of amorphous precursor dust can produce a range of chemical compositions of ultrafine-grained minerals and (non-equilibrium) mineral assemblages and textures in dust contained in comet nuclei as a function of period and trajectory of orbit and number of perihelion passages (not considering internal heating). Thus, experimental data on relevant processes and reaction rates between 200 and 400K are needed in order to evaluate comet selection, penetration depth for sampling device and curation of samples for CNSRM.

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